DOCKET NO: 242136US0DIV

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF   :

YOSHIHIRO FUJIMORI, ET AL.   : EXAMINER: ACQUAH, S. A.

SERIAL NO: 10/650,790   :

FILED: AUGUST 29, 2003   : GROUP ART UNIT: 1711

FOR: POLYESTER RESIN AND PROCESS FOR ITS PRODUCTION:

DECLARATION UNDER 37 C.F.R. § 1.132

COMMISSIONER FOR PATENTS
ALEXANDRIA, VIRGINIA 22313

SIR:

        Now comes __Yoshihiro Fujimori_____ who deposes and states:

        1. That I am a named inventor of the present application.

        2. That I am a graduate of _Tokyo University_____ and received a __Master's

degree in the year _1993_ in the field of _Chemistry_____.

        3. That I have been employed by _Mitsubishi Chemical Corporation , for _12_ years

as a _Research Scientist and Technical Manager_ in the field of _Polyester_.

        4. That in the Office Action mailed on January 11, 2005, the Examiner improperly

maintained the rejection over Hilbert et al. The Examiner appears to base his rejection on his

interpretation of Example 4 of this reference as disclosing a titanium-containing compound at

a stage for transportation to a melt polycondensation step. It appears that the Examiner's

position is based on the fact that the titanium-containing compound is contacted with an

esterification reaction product (PET) prior to melt condensation. However, this assertion by

the Examiner is incorrect.

In particular, the Examiner has apparently overlooked the fact that in Example 4 of Hilbert et al the titanium-containing compound is added *to the polycondensation tank* and not "the esterification reaction tank for a final stage in a multi-stage reaction apparatus or to an esterification reaction or ester exchange reaction product in a stage for transportation to a melt polycondensation step" as is presently claimed.

The Examiner attempts to compensate for this deficiency in the disclosure of Hilbert et al stating: "for example, in a continuous process, the reaction product from the esterification is transported to the polycondensation step. The preparatory step in between clearly satisfy the requirements of the claims." Again, this assertion is unfounded as the process disclosed in Example 4 of Hilbert et al is *not* a continuous process.

To obtain a better appreciation for the differences between the presently claimed method and that described by Hilbert et al, as well as the unexpected advantages flowing therefrom, the Examiner is directed to paragraph 6 below (especially the "Analysis" section).

5. That the following experiments were carried out by me or under my direct supervision and control to demonstrate the advantages flowing from the claimed invention. Specifically, the following data demonstrate the advantageous properties that flow from the following difference in the disclosure of Hilbert et al and the presently claimed invention: in Hilbert et al, as represented by Example 4, the titanium-containing compound is added *to the polycondensation reaction tank* and not "the esterification reaction tank for a final stage in a multi-stage reaction apparatus or to an esterification reaction or ester exchange reaction product in a stage for transportation to a melt polycondensation step" as presently claimed.

The differences between the present invention and that disclosed by Hilbert et al are presented in the following Table A:

Table A: Differences between the present invention and Hilbert et al

Item	Hilbert et al - Example 4	Present Application, Claim 16
Addition point	Polycondensation tank	Esterification tank or stage for transportation

A. Revival of U.S. 6,667,383[1] Example 4

Melt polycondensation was carried out in accordance with the description of Column 14 to 15 and Table 1 of the printed patent (shown below as Table B). The melt polycondensation time (the period from the starting point of pressure reduction to the point when intrinsic viscosity come to 0.55dl/g) was 3.78 hr.

Slurries of 43 kg (260 mol) of terephthalic acid and 19 kg (312 mol) of ethylene glycol were continuously supplied over a period of 4 hours to an esterification reaction tank having about 60 kg of bis(hydroxyethyl) terephthalate previously charged and maintained at a temperature of 250° C. and a pressure of 1.2×10^5 Pa, and even after completion of the supply, the esterification reaction was further carried out for one hour. About one half of this esterification reaction product was transferred to a polycondensation tank.

Then, to the polycondensation tank to which the esterification reaction product was transferred, from its pipe, ethyl acid phosphate, magnesium acetate and tetra-n-butoxy titanium were sequentially added in their ethylene glycol solutions, respectively, with intervals of 5 minutes, so that 0.194 mol of phosphorus atoms (P), 0.123 mol of magnesium atoms (Mg) and 0.063 mol of titanium atoms (Ti) would remain per 1 ton of the resulting polyester resin. Then, the interior of the system was heated from 250° C. to 280° C. over a period of 2 hours and 30 minutes, and at the same time, the pressure was reduced from normal pressure to 4×10^2 Pa over a period of one hour, and while maintaining the same pressure, melt polycondensation was carried out for a period of time until the intrinsic viscosity of the obtained resin became 0.55 dl/g. The

---

[1] This patent was issued in parent application U.S. 10/263,716 filed on October 4, 2002. For sake of convenience, the Examples listed in Section 4A refer to the issued patent; however, all designated sections may be found in the specification of the present application.

polymer was withdrawn in the form of a strand from the
discharge outlet provided at the bottom of the polycondensation
tank, cooled with water and then cut into chips to obtain about
50 kg of a polyethylene terephthalate resin.

Subsequently, solid state polymerization test was carried out in accordance with the
description of column 21, example 9.

Then, the polyester resin chips obtained as described above
were continuously supplied for crystallization to an agitation
crystallization machine held at about 160° C. in a nitrogen
atmosphere so that the retention time would be about 60
minutes and then continuously supplied to a tower type solid
polycondensation apparatus and heated at 205° C. in a nitrogen
atmosphere for 25 hours for solid phase polycondensation by
adjusting the retention time so that the intrinsic viscosity ($[\eta_2]$)
of the obtained polyester resin would be 0.75 dl/g. The
intrinsic viscosity ($[\eta_1]$) of the above melt polycondensate resin
and the intrinsic viscosity ($[\eta_2]$) of the solid polycondensate
resin, were measured by the above-mentioned method.

Then, melt polycondensation rate V1 and solid polycondensation rate V2 are
calculated in accordance with the description of column 21, example 9, that is:

Further, the melt polycondensation rate (V_1) as a value obtained
by dividing the intrinsic viscosity ($[\eta_1]$) of the above melt
polycondensate resin by the melt polycondensation time, the
solid phase polycondensation rate (V_2) as a value obtained by
dividing the difference ($[\eta_2]-[\eta_1]$) between the above intrinsic
viscosity ($[\eta_2]$) of the above solid polycondensate resin and the
intrinsic viscosity ($[\eta_1]$) of the above melt polycondensate resin,
by the solid phase polycondensation time, and the ratio (V_2/V_1)
of the solid phase polycondensation rate (V_2) to the melt
polycondensation rate (V_1), were calculated, respectively, and
the results are shown in Table 2.

The result is: V1=0.146, V2=0.008, V2/V1=0.055.

B. Reference Example based on Example 1-4-5 of U.S. 5,886,133 (Hilbert et al)

Melt polymerization and solid phase polymerization were performed in the same
manner as described above for Example 4 of U.S. 6,667,383 (*i.e.*, addition of the Ti catalyst

to the polymerization tank). However, the amounts of catalyst added were changed to be consistent with those used in example 1-4-5 of Hilbert et al[2]. Specifically, the following amounts of catalyst were used:

Ethyl acid phosphate: 0.194 mol of phosphorus atoms (P) per 1 ton of the resulting polyester resin.

Tetra-n-butoxy titanium: 0.101 mol of titanium (Ti) per 1 ton of the resulting polyester resin.

As described above for Example 4 of U.S. 6,667,383, and in accordance with column 21, example 9 therein, the melt polycondensation rate V1 and solid polycondensation rate V2 were calculated. The result was: V1=0.168, V2=0.0061, V2/V1=0.036.

6. Results and analysis:

The difference between the addition method represented by Example 4 of Hilbert et al[3] and the addition method defined in pending Claim 16 is shown in the following Table 1 from the printed patent (represented as Table B), which compares the Hilbert et al method with that set forth in Examples 4 and 10 in U.S. 6,667,383.

Table B: Table 1 from U.S. 6,667,383

			Catalyst was added to the polycondensation reaction tank	Cited reference	Present application
			US 6,667,383 Example 4	US 5,886,133 Example 1-4-5	US 6,667,383 Example 10
Addition point of Compound(1)			polycondensation tank		Stage for transportation
Contents of metal atoms	Titanium atoms(T)	(mol/t)	0.063	0.104	0.063
	Magnesium atoms(M)	(mol/t)	0.123	-	0.123
	Phosphorus atoms(P)	(mol/t)	0.194	0.194	0.194

[2] Example 1-4-5 is an annotation utilized in recognition of the fact that the TPA based PET oligomer used in Examples 4 and 5 is that prepared in Example 1 and that the solid state polycondensation experiment in Example 5 of Hilbert et al utilizes the PET precursor described in Example 4.
[3] Designated as Example 1-4-5 of Hilbert et al.

	M/T		1.95	0	2.0
MSP	IV	(dl/g)	0.55	0.58	0.56
	Melt polycondensation time	(hrs)	no description **3.78**	**3.45**	3.33
	Polycondensation rate(V1)	(dl/g/hr)	no description **0.146**	**0.168**	0.168
Resin chips	Intrinsic Viscosity[η]	(dl/g)	0.74	0.71	0.75
	Solid phase polycondensation time	(hrs)	no description **205°C 25:00**	222-3°C 4:38 205°C **28:00**	205°C 20:00
	Polycondensation Rate(V2)	(dl/g/hr)	no description **0.008**	**0.0061**	0.010
	V2/V1		no description **0.055**	**0.036**	0.060
	Color coordinate b		+2.4	no description	+2.4
	Acetaldehyde Content(AA1)	(ppm)	no description	no description	4
	Cyclic trimer(CT)	(ppm)	0.29	no description	0.28
	Absorbance	395nm	0.14	no description	0.14
		500nm	0.02	no description	0.02
Stepped Molded plate	Temperature-rising crystallization temperature(Tc)	(°C)	172	no description	no description
	Acetaldehyde content (AA2)	(ppm)	no description	no description	18
	Haze	(%)	no description	no description	8
Bottle	Aroma-retention Property		○	no description	○
	Mold contamination Property		○	no description	○
	Acetaldehyde odor		no description	no description	4

Analysis-

Since Example 4 of U.S. 6,667,383 gives no specific disclosure about the "melt condensability" and "solid phase polycondensability", by performing the experiments described herein above, we add the data of these parameters in the above Table B (bold and underlined portion). Further, we have made a repeating experiment of Example 1-4-5 of U.S. 5,886,133 (Hilbert et al.), and then conducted various evaluations in accordance with the disclosure of U.S. 6,667,383, and compared the data of "melt condensability" and "solid

phase polycondensability" from those of the present application. The results are also indication in the above Table B.

At first, when the Ti catalyst was added to the "stage for transportation" in accordance with the method of present Claim 16 (Example 10 of US 6,667,383), the solid phase polycondensation was improved by about 25% (polycondensation rate (V2): 0.008 → 0.010) as compared with the case where using the completely same catalyst composition, the Ti catalyst was added to the polycondensation tank (Example 4 of US 6,667,383). This means that the productivity was improved by about 25% and substantially significant difference was brought about in an industrial application.

It is also evident from the aforementioned results that when the method of the present invention is compared with the method (Example 1-4-5) of US 5,886,133 (Hilbert et al.), although the Ti catalyst amount of the present invention is small (titanium atoms (T): 0.104 → 0.063), the solid phase polycondensability was further improved in the present (polycondensation rate (V2): 0.0061 → 0.010) (improved by at least 50%). And, as the results, the balance V2/V1 of the solid phase polycondensation rate and the melt polymerization rate was substantially improved.

Such relationship between the point of adding the catalyst and the effect of improving the polymerizability is described in column 11, lines 16 to 24 of US 6,667,383 issued on the parent application. The results above are neither disclosed, suggested, nor expected from the disclosure of Hilbert et al.

The reason why the effects of improving the polymerization properties can be improved by the difference in the point of addition was not clear at the time of filing the present application, and details thereof are still unclear. However, as a tentative theory, it is

conceivable that the improvement can be obtained by the difference in the properties of the oligomer to which the catalyst is added.

Namely, even if a PET oligomer is not subjected to a polycondensation step, its esterification ratio (ratio that the terminal of a carboxylic acid is esterified by glycol) and the polymerization degree tend to increase as the time passes only by maintaining the heating operation. It is considered that, in the "polycondensation tank," the esterification ratio and the polymerization degree are higher than those in the "esterification tank" and "stage for transportation." In Example 4 of Hilbert et al wherein an oligomer obtained according to the process described in Example 1 therein the steps of removal, cooling and grinding are charged in a reaction tank (vessel) together with a catalyst and additives, and then heating and polycondensation are performed. Therefore, there is a possibility that the esterification ratio and the polymerization degree increase to a great extent in a heating stage before polycondensation, that is a step until the oligomer is re-melted and becomes active.

Alternatively, in Example 4 of US 6,667,383, there is a possibility that at the time when an esterification product is transported to the polycondensation tank, its esterification ratio and polymerization degree might be already higher than those in the "esterification tank" and "stage for transportation," and under such circumstance a Ti compound is added thereto. As such, it seems that the Ti compound is preferably added at such a stage that the esterification ratio and polymerization degree are relatively low, in order to improve the polymerization rate. The catalytic functions of a catalyst for PET, particularly a Ti catalyst, tend to substantially vary by even a slight difference in the esterification ratio and polymerization degree of the product to be added.

As another tentative theory, an influence of monomers is conceivable. Namely, in Example 4 of Hilbert et al terephthalic acid and ethylene glycol monomers were charged in a

tank (vessel) in Example 1 and the raw material oligomer used in Example 4 was prepared in this tank. Accordingly, the monomers, even in a slight amount, remain as they are in the oligomer, and there is a strong possibility that such monomers might be mixed and directly contacted with a Ti compound in Example 4.

On the contrary, in the multi-stage reaction apparatus as defined in Claim 16 of the present invention, as is apparent from Example 10 or the drawing attached herewith, the reaction tank in which terephthalic acid and ethylene glycol are charged is *different from* the reaction tank in which a Ti compound is added or a transportation pipe, and therefore the monomers have virtually no direct contact with a Ti catalyst. Namely, by carrying out the esterification in a multi-stage system, it is possible to ultimately avoid the direct inclusion of monomers at the time of adding the catalyst. The monomer having a carboxylic acid group such as terephthalic acid easily reacts with a metal compound to form a metal salt and deactivates the catalytic function of a Ti compound. As a result, there is a possibility that such an operation might be seen as the difference in the productivity as indicated in the above Table B.

Namely, it is considered that by adding a Ti compound *"to an esterification reaction tank for a final stage in a multi-stage reaction apparatus or to an esterification reaction or ester exchange reaction product in a stage for transportation to a melt polycondensation step,"* it is possible to add the Ti compound to an oligomer of which the inclusion of monomers is small, although the esterification ratio and polymerization degree are relatively low thereby providing the aforementioned beneficial effects for improving the polymerization rate.

9

Although the aforementioned discussion proffers tentative theories, it is evident from the results above in Table B that unexpected large effect is given to the productivity by the difference of the point of addition.

The Examiner state that "the stage of the polyester preparation between esterification and polycondensation ... is part of the final stages of esterification or is likewise, part of the preparation steps (of polyester) for polycondensation" on page 2, lines 19 to 22 of the Office Action dated January 11, 2005. However, Hilbert et al have not disclosed or suggested such a equivalence in timing as the Examiner has asserted. It should also be understood that, as explained above, the preparation step of polyester between the esterification and the polycondensation is a very important part and cannot be said to be a final stage for esterification or a part of a preparation step for polycondensation.
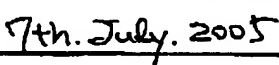
Accordingly, for the foregoing reasons, the presently claimed process and the method described in Example 4 of Hilbert et al are different, and flowing from this difference is the unexpected results summarized in Table B.

7. The undersigned petitioner declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing therefrom.

8. Further deponent saith not.

_____
Signature   Yoshihiro Fujimori

_____
Date   7th. July. 2005

10